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Variations of carbon monoxide density in the total atmospheric column over Russia between 1970 and 1995: Upward trend and disturbances, attributed to the influence of volcanic aerosols and forest fires

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Abstract. The analysis of total column spectroscopic CO observations over Russia revealed an upward linear trend between 1970 and 1995 with a rate of about 1.0 ppbv/year or 0.96 %/year. A similar trend was reported earlier for the CO total column over Switzerland between 1950 and 1987. This rate is almost 3 times higher, than the rate of CO increase between 1920 and 1950, obtained from ice core data. Main disturbances of CO tropospheric concentration coincided with vast wildfires in the central Russia in 1972 and volcanic eruptions. Stratospheric volcanic aerosol probably influence the concentration of tropospheric OH radicals, which destroy CO molecules. The aerosol scatters photochemically active UV radiation and, in the same time, triggers the stratospheric ozone photochemical destruction. Diminished total column ozone UV absorption can offset the increase of UV scattering due to additional aerosol. Studying these processes is important for a prediction of further CO and OH long-term variations in the global atmosphere.

Introduction

Carbon monoxide (CO) is a quite variable trace gas, which is strongly influenced by human activity and photochemical processes.

Human activity is responsible for about half of the CO input in the Northern Hemisphere (NH). In addition several natural processes, most important of which are forest fires and oxidation of methane and other hydrocarbons, contribute to the CO cycle. A reaction between CO and OH is the major sink for both CO and OH [*Mueller and Brasseur,* 1995]. Radical OH in turn is the main oxidizing agent in the background troposphere, representing, for example, more than 80% of the total sink for atmospheric methane, a very important greenhouse gas. Radical OH is a product of photochemical reactions in the troposphere.; [OH] depends on UV radiation flux and the concentrations of ozone, NOx, water vapor, CO and other trace gases and radicals [*Mueller and Brasseur,* 1995].

A first rough estimate of CO long-term trend for background NH air was obtained by *Dianov-Klokov and Yurganov* [1981] from a comparison of total column spectroscopic measurements in Zvenigorod, near Moscow in 1970-1976 to those conducted by *Shaw* [1958] in Columbus, Ohio, in 1952-1953; no change for summer months and a 2%/year increase for January-April was found. A difference in location of these two sites, different processing techniques, urban contaminations, and an influence of wildfires in summer 1952 and summer 1972 made this estimate uncertain. A similar approach was used by *Zander et al.* [1989], but they applied uniform retrieval procedures to spectra recorded in the same place, the high altitude station Jungfraujoch, Switzerland, in 1950-1951 and in 1985-1987; their estimate was 0.85 ± 0.20 %/year. *Dvoryashina et al.* [1984] estimated the trend in Zvenigorod between 1970 and 1982 to be 1.4 and 1.7 %/year for summer and winter, respectively. *Khalil and Rasmussen* [1984] found that the surface CO concentration at Cape Meares (45° N) between 1979 and 1983 rose at the rate of 6%/year. However, their estimate for the period 1979-1986 and for a larger number of stations was lower: 0.8 ppbv/year for both hemispheres [*Khalil and Rasmussen,* 1988].

A stabilisation or even a decrease of [CO] was reported for the period after 1983-1987. No increase was observed between 1983 and 1993 in Zvenigorod (-0.08 ± 0.5%/year, according to *Yurganov et al.* [1995]). Flask samples of surface air revealed even a decrease in CO concentration. *Khalil and Rasmussen* [1994] found rates of -1.3 ppbv/year in the NH and -2.3 ppbv/year in the Southern Hemisphere (SH) between 1987 and 1992. *Novelli et al.* [1994] reported rates of -7.7 and -3.7 ppbv/year for NH and SH, respectively, for a shorter period between 1990 and 1993.

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Several hypotheses have been proposed to explain this behavior of carbon monoxide. A decline of the rate of man-induced CO emission after 1983 has been postulated [*Khalil and Rasmussen,* 1994; *Novelli et al.,* 1994]. An increase of [OH] due to stratospheric ozone depletion and an increase in UV flux after 1982 were considered to play a role in the reduction of the rate of increase of CO and methane [*Madronich and Granier,* 1992; *Yurganov,* 1993]. [OH] decrease due to a screening of the troposphere from solar UV radiation by the Pinatubo volcanic sulfate aerosol was proposed by *Dlugokencky et al.* [1996] as an explanation for tropical and SH [CO] variations around 1991.

To our mind almost all the proposed mechanisms influence tropospheric CO. This paper focuses on two phenomena, connected with volcanic eruptions: an increase of stratospheric aerosol and a decrease of stratospheric ozone induced by the aerosol. The stratosphere plays a role of a filter for photochemically active UV radiation; the transparency of the filter depends on the stratospheric composition.

Results and Discussion

Zvenigorod spectroscopic data (56° N, 37° E, 200 m asl) for 1970-1986 were published by *Dianov-Klokov and Yurganov* [1989], and, updated to 1993, by *Yurganov et al.* [1995]. The processing technique, described by *Dianov-Klokov and Yurganov.* [1989], was based on the R(3) line of CO fundamental band, measured in the absorption spectrum of the entire atmosphere using the sun as a light source. Total column CO amount (*e.g.*, in mol/cm^2) is expressed here as weighted average mixing ratio for the entire atmosphere in parts per billion by volume (ppbv). For typical vertical CO profiles the weighted average is very close to the mixing ratio, averaged over the tropospheric layer [*Dianov-Klokov and Yurganov* 1989, *Yurganov et al.,* 1997]. The precision of a single measurement is ± 5-6%. As a rule 15-25 spectra per day were observed, therefore a statistical uncertainty of the daily average was around ± 1%. Monthly means were obtained, as a rule, from data of 5-20 sunny days ; they have a precision of ± 3-5%, determined by natural day-to-day variability of CO abundance with a magnitude of ± 10-12% [*Yurganov et al.,* 1995].

The measured monthly mean [CO] as a function of time t can be considered as a composition of three components [*Khalil and Rasmussen,* 1995]:

$$[CO](t) = T(t) + S(t) + D(t) \qquad (1)$$

where T is a trend (which is assumed to be linear here); S is a regular seasonal deviation (being the function of month and assumed to be the same for all the years); D is an irregular disturbance (a "residual", which is not described by the trend and seasonal cycle).

Monthly mean CO mixing ratios in ppbv for the period 1970-1995 are presented in Figure 1 and are given also in the Electronic Data Supplement[1]. Between 1977 and 1979 the measurements were not conducted. First the data were smoothed by a simple 12-month running averaging to exclude the seasonal cycle. This procedure seems not quite correct: during some months (*e.g.*, some of Novembers and Decembers) measurements were not possible because of weather and/or short sunny time during the day. These yearly averages should depend on which and how many months were missing. Therefore, another procedure of excluding seasonal variations was applied. First, all the available data were averaged by months regardless of the year. Then the overall average mixing ratio, 122.2 ppbv, was subtracted from the obtained monthly means, and the mean seasonal deviations from the annual average $S(t)$ (here t is a month of the year) were determined. Deseasonalized monthly means were obtained by subtracting $S(t)$ from $[CO]$.

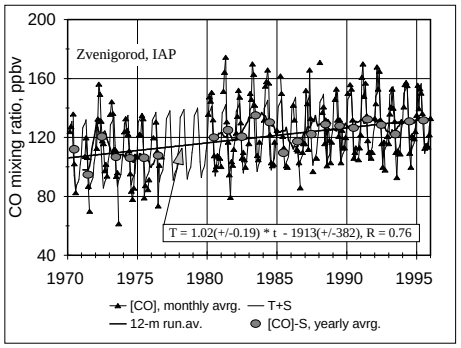

Figure 1. Vertically averaged CO mixing ratio ([CO]) over Zvenigorod, Russia, as a function of time t (the time ticks in all the figures correspond to January 1 of the designated year). In the box is linear trend $T(t)$, R is the correlation coefficient, S is the seasonal cycle (see text).

The deseasonalized annual averages ($[CO] - S$), representing $T + D$ (see equation (1)) have been plotted in Figure 1 by circles. The straight line is the simple linear regression derived from them (the trend T). The thin periodical broken line is $T + S$, calculated as described above.

Figure 1 clearly demonstrates an upward trend for both yearly means, deseasonalized as described above, (circles) and for the simplest 12-months running smoothing of data with gaps (thick broken line). The slope of the regression line, calculated from the deseasonalized data is 1.02 ppbv/year. This rate corresponds to 0.96 ± 0.18 %/year if we divide it by the mean [CO] in 1970, 106.2 ppbv. It can be noted that the trend of total column CO over Russia for 1970-1995 is in excellent agreement with the trend of total column CO amount, spectroscopically measured by *Zander et al.* [1989] for

[1]The Electronic Data Supplement is available on diskette or via Anonymous FTP from kosmos.agu.org, directory APEND (Username=anonymous, Password=guest). Diskette may be ordered by mail from AGU, 2000 Florida Ave., NW, Washington, DC 20009 or phone at 800-966-2481: $15.00. Payment must accompany order.

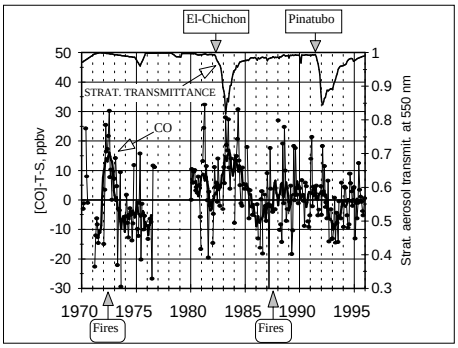

Figure 2. Monthly mean detrended and deseasonalized mixing ratios $[CO] - T - S$ (points) and 9-months running average (solid curve). Upper curve is the transmittance of stratospheric aerosol at wavelength 550 nm, $T_s = \exp(-\tau)$, optical depths τ for 58.7° N are taken from *Hansen et al.* [1996].

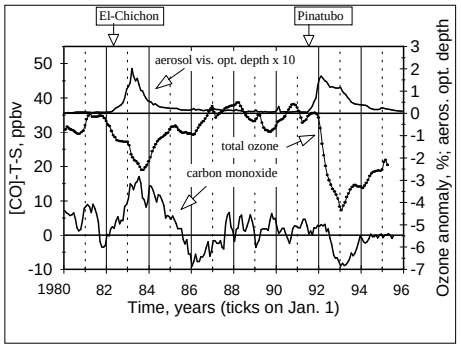

Figure 3. Detrended and deseasonalised smoothed [CO] in Zvenigorod (bottom curve) in comparison to zonally averaged total ozone anomalies for 55° N (also detrended), middle curve; and aerosol visible optical depth τ for 58.7° N, top curve.

the period 1950-1987: 0.85 ± 0.20 %/year.

This CO growth is 3 times steeper than that between 1920 and 1950 (0.35 ppbv/year), assessed from the analysis of old air preserved in Greenland ice [*Haan et al.,* 1996]. An apparent acceleration can be explained by an enormous economic growth after World War II, as it was speculated by *Khalil and Rasmussen,* 1995 for similar features for carbon dioxide and methane time series.

To clarify the disturbances both trend T and seasonal cycle S were subtracted from [CO], Figure 2, points. A smoothing (the thick line) has been performed by a 9-month running averaging, because the seasonal cycle had been removed already and 12-month smoothing was not necessary.

The disturbance of 1972 may be explained by wildfires: a strong drought in 1972 caused catastrophic forest and peat fires in the European part of Russia [*Kats,* 1974]. However, severe forest fires, which occurred in northern China and south-eastern Siberia in 1987 [*Cahoon et al.,* 1994] did not impact CO measured by us near Moscow. The effects of diluting emissions and photochemical CO destruction, which is effective in summer, as well as prevailing West-East atmospheric transport, probably, can explain this difference.

Two great eruptions, which caused enhancements of the stratospheric aerosol on a global scale, happened during this period: Mt. El-Chichon in April, 1982 and Mt. Pinatubo in June, 1991. The maximum depletions of the radiation flux near 550 nm at northern mid latitudes due to a scattering by the stratospheric aerosol amounted to 15% (upper curve in Figure 2). The UV radiation at 300-310 nm should be similarly scattered by the aerosol, and [OH] should be depleted [*Madronich and Granier,* 1992]. The CO enhancement over Zvenigorod of 1982-1983 and following relaxation of 1984-1985 may be caused by this [OH] disturbance; the CO record follows the radiation curve with a small time lag. But for the Pinatubo case the pattern seems to be quite different: a [CO] decrease instead of increase was observed in 1991-1992.

The different responses of CO in Zvenigorod to these two volcanic events require a consideration of additional mechanisms . As was shown by *Solomon et al.* [1996] (and references therein), volcanic aerosol particles trigger photochemical heterogeneous reactions, which destroy ozone molecules in the lower stratosphere. The total ozone zonally averaged anomalies, measured by TOMS (version 6) and calculated as percentage differences from the 1987-1990 mean [*Randel et al.,* 1995] were compared with our CO data. They were smoothed by *Solomon et al.,* [1996](personal communication of S.Solomon) using a simple 25-month running averaging. Ozone linear trend with the rate of -0.46 % per year was subtracted by us to make possible a comparison with the detrended CO (Figure 3).

It seems, that at least two competing mechanisms influence UV radiation: scattering by stratospheric aerosol and absorption by stratospheric ozone. Volcanic aerosol deplets ozone, this depletion increases UV flux and offsets the UV depletion, caused by aerosol scattering. Aerosol scattering appeared to prevail during the El-Chichon event, but ozone depletion prevailed during the Pinatubo event. In this respect, a coincidence of CO and aerosol maxima in 1983 as well as CO and ozone minima in 1993 are noteworthy.

Thus, in terms of longer time scale both possible long-term stratospheric aerosol trend [*Hoffman,* 1990] and total column ozone depletion[*Randel et al.,* 1995] should be taken into account for CO trend analysis and predictions. A long period of consistent measurements is necessary to make a conclusion on long-term changes of this trace gas.

Conclusions

1. Carbon monoxide total column amount time series, obtained in Zvenigorod, in the European part of Russia, can be represented by a trend, seasonal cycle and disturbance components. Linear trend during 1970-1995 amounted to 1.02 ± 0.19 ppbv/year or 0.96 %/year.

This trend is close to the estimate of *Zander et al.,* [1989] for 1950-1987. A comparison with ice core data allows one to assume a CO acceleration between 1920-1950 and the present time.

2. Eruptions of El-Chichon and Pinatubo volcanoes appeared to influence CO abundance above Zvenigorod. However, [CO] was changing after these eruptions different ways: it increased after the first one and decreased after the second one. This can be explained by different net changes in UV flux and tropospheric OH concentrations after these eruptions. UV depends not only on the scattering by stratospheric volcanic aerosol, but also on ozone absorption. The ozone depletion after Pinatubo event appeared to be more considerable than after El-Chichon eruption. Biomass burning in central Russia in summer of 1972 enhanced CO mixing ratio too.

3. Variations of stratospheric aerosol and total column ozone influence tropospheric CO and, probably, tropospheric OH; they should be taken into account in prognostic models.

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